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A NEW CLASS OF CATION CONDUCTORS: POLYPHOSPHAZENE
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A New Class of Cation Conductors:

Polyphosphazene Sulfonates

by

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ABSTRACT

The phosphazene polyelectrolytes, $[NP(OR)_x(OC_2H_4SO_3Na)_{2-x}]_n$ [R = $C_2H_4OC_2H_4OCH_3$; x = 1.54, 1.75 and 1.80 (3-5); R = C_2H_4O]_{7.22}CH₃, x = 1.80 (6)] were synthesized and characterized. The synthetic procedures were developed first through the use of hexachlorocyclotriphosphazene as a small-molecule model system. The polyelectrolyte 6 shows a conductance of $1.7 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 80 °C.

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A NEW CLASS OF CATION CONDUCTORS:

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↙ In recent years there has been considerable interest in the mechanism of charge transport in solvent-free polymer electrolytes and in the potential application of these electrolytes in electrochemical devices.¹⁻³ Most attention has been paid to polymer electrolytes formed from linear-chain polyethers, poly(ethylene oxide) or poly(propylene oxide) with alkali metal salts. Recently, polymer electrolytes based on phosphazene and siloxane comb polymers have been reported which exhibit better conductivity at room temperature than for the linear-chain polyether electrolytes.⁴⁻⁶ The high conductivity of these materials arises from their highly flexible polymer segments. A drawback for most polymer electrolytes is that the transference number for the cation lies in the range 0.3 to 0.5. In order to increase the fraction of the charge carried by the cation, we have experimented with polymers in which the anion is covalently attached to the polymer (polyelectrolytes). Conventional polyelectrolytes are rigid materials in the absence of solvent, however, we have shown that certain plasticizers greatly improve the conductivity of polymers such as sodium poly(styrene sulfonate), and we suggested that polyelectrolytes that

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incorporate flexible groups by covalent bonds would be a logical next step.^(7,8) This more elegant approach was realized by LeNest and coworkers who synthesized a polyelectrolyte based on crosslinked ether networks containing phosphate charged groups.⁹ Conference reports of other flexible polyelectrolytes also have appeared.¹⁰ Also, the electrical properties of a polyether-polyelectrolyte blend has been investigated.¹¹ In this communication we report the synthesis and conductivity of a new class of polyelectrolytes having phosphazene backbone and with sulfonate and oligoether side chains.

As a model system for the analogous reaction with linear poly(dichlorophosphazene), $[\text{NPCl}_2]_n$, we investigated the equimolar reaction of hexachlorocyclotriphosphazene, $\text{N}_3\text{P}_3\text{Cl}_6$, with the disodium salt of 2-hydroxyethanesulfonic acid $\text{NaOC}_2\text{H}_4\text{SO}_3\text{Na}$, in THF in the presence of 15-crown-5. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture shows two sets of an A_2B pattern [set i: 22.2 ppm (d), 0.5 ppm (t), $^2J(\text{PP}) = 45$ Hz and set ii: 22.8 ppm (d), 3.9 ppm (t), $^2J(\text{PP}) = 66$ Hz] in the intensity ratio 3:2. The chemical shift and intensity of the signals suggest that the products should be assigned as compounds 1 and 2: The ^{31}P NMR assignments for 2 were confirmed by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product obtained from the equimolar reaction of $\text{N}_3\text{P}_3\text{Cl}_6$ with sodium ethanesulfonate, $\text{NaC}_2\text{H}_5\text{SO}_3$; an A_2B pattern, 21.8 ppm (d), 3.4 ppm (t); $^2J(\text{PP}) = 64$ Hz consistent with a monosubstituted derivative, $\text{N}_3\text{P}_3\text{Cl}_5(\text{OSO}_2\text{C}_2\text{H}_5)$. Thus, the alkoxy sulfonate acts as a difunctional reagent towards $\text{N}_3\text{P}_3\text{Cl}_6$. Surprisingly, the sulfonate is sufficiently nucleophilic to displace chlorine atoms from the $=\text{PCl}_2$ center.

In THF the dinegative compound, $\text{NaOC}_2\text{H}_4\text{SO}_3\text{Na}$, reacts with an excess of

linear $[\text{NPCl}_2]_n$ in the presence of 15-crown-5 to produce a partially substituted product (Scheme 1). The reaction mixture was then treated with the sodium salt of 2-(2-methoxyethoxy)ethanol or poly(ethylene glycol methyl ether) of average molecular weight 350 to yield derivatives of polyphosphazene sulfonates. The objective of this reaction was to displace the sulfonate groups attached to phosphorus atoms.¹² Also, any cross-linking by the alkoxy sulfonate is removed in this process [Scheme I step (ii)]. Independent experiments confirmed that the alkoxide ion displaces sulfonate groups. For example, treatment of compounds 1 and 2 with excess sodium alkoxide produced $\text{Na}[\text{N}_3\text{P}_3(\text{OR})_5(\text{OC}_2\text{H}_4\text{SO}_3)]$ and $\text{N}_3\text{P}_3(\text{OR})_6$ ($\text{R} = \text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OCH}_3$) respectively.

The ^{31}P , ^1H NMR, and IR spectra for the resulting polymers indicate total halogen replacement.¹³ The ratio of the sulfonate group to the ether side groups is established by the ratio of the integral intensities of OCH_2 protons with CH_2S protons from ^1H NMR spectra. In addition, qualitative tests using Ag^+ demonstrated the lack of appreciable chloride in the product. The amount of sulfonate groups incorporated in the polymer backbone is generally 50% of that initially used in the reaction. The advantages of this synthetic procedure are that the length of the ether side groups and the ratio of the sulfonate groups to ether groups can be easily varied. Presumably the substitution reactions do not occur in a stereo regular manner.

The following polymers $[\text{NP}(\text{OR})_x(\text{OC}_2\text{H}_4\text{SO}_3\text{Na})_{2-x}]_n$ [$\text{R} = \text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OCH}_3$, $x = 1.54, 1.75$ and 1.80 (3-5); $\text{R} = (\text{C}_2\text{H}_4\text{O})_{7.22}\text{CH}_3$, $x = 1.80(6)$] were prepared to test the influence of charge concentration on ion transport. The value of 7.22 for the number of OC_2H_4 repeat unit reflects the average molecular

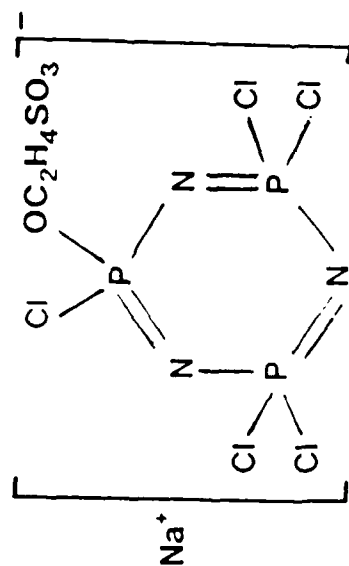
weight of the poly(ethylene glycol) starting material. Anal.¹⁴ calcd. for 4: C, 38.28; H, 7.03; N, 4.83; Found: C, 36.06; H, 6.61; N, 6.22. Calcd. for 6: C, 48.18; H, 8.34; N, 1.99; Found: C, 46.13; H, 7.63; N, 2.78. The phosphazene polyelectrolytes with high sulfonate concentration are rigid solids whereas the polymers 4 and 5 are elastomers at room temperature. Ionic conductivities were measured by complex impedance spectroscopy¹ in the frequency range $10\text{--}3 \times 10^6$ Hz, using stainless steel electrodes. Gentle curves were obtained when $\log \sigma$ is plotted against $1/T$ (Fig. 1), as expected for ion transport in amorphous polymers.^{3,15} The conductivities observed for the above polymers are comparable to values recently reported by Cheradame's group for polyether phosphates.⁹ The general synthetic procedure employed here should permit the attachment of a wide variety of pendant charged groups to the phosphazene backbone. A detailed study is underway on other charged groups and on the dependence of conductivity on charge concentration.

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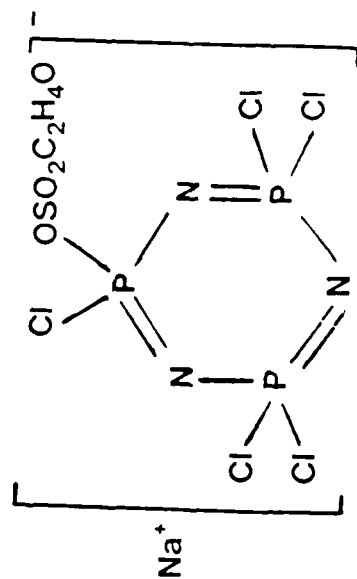
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13. ^{31}P NMR: 4 to -6 ppm (br) ($\text{H}_3\text{PO}_4/\text{D}_2\text{O}$). Broadness decreases as the amount of sulfonate groups in the polymer backbone decreases. ^1H NMR: 3.4 to 4.1 ppm for OCH_2 protons and a broad peak at 1.9 ppm for SCH_2 protons [$\text{D}_2\text{O}/\text{TMS}$ (ext.)]. IR: 1210 - 1280 $\text{cm}^{-1}(\text{b})$ for $\nu(\text{P}=\text{N})$, 1050 - 1100 $\text{cm}^{-1}(\text{b})$ for $\nu(\text{SO}_3\text{Na})$.
14. Stoichiometry of polyphosphazene sulfonate is taken from the integral intensity ratios of appropriate peaks from the ^1H NMR spectra.

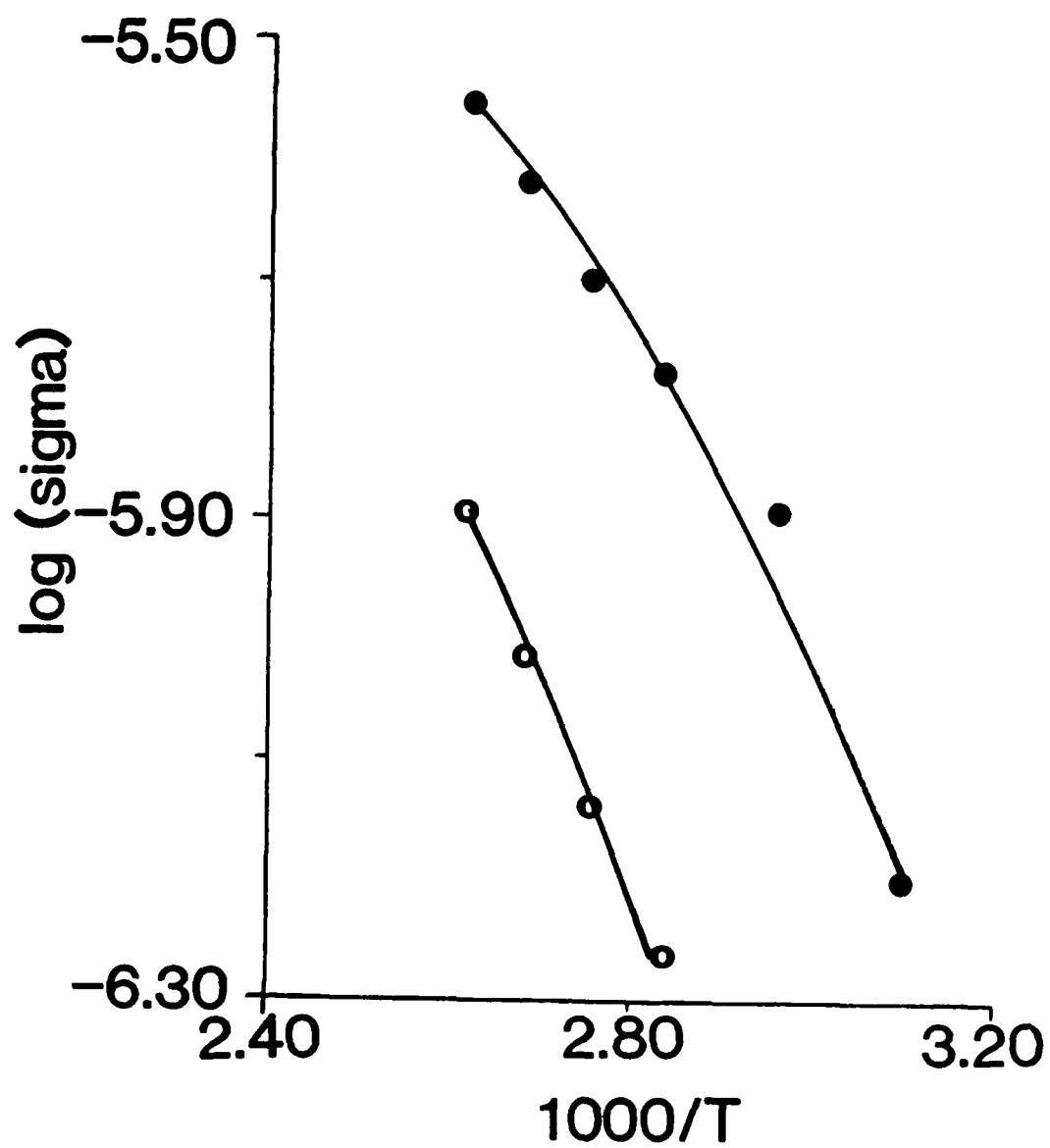
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